μ-(Carbonyltriphenylphosphineplatinio)octacarbonyldi-iron: an Unusual Platinum–Iron Cluster Complex

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Summary The synthesis and structural chemistry of $Ph_3P(CO)PtFe_2(CO)_8$ is described and related to similar cluster complexes.

The reaction of PtL_4 (L = tertiary organophosphine) or L_2Pt(olefin) with $Fe_3(CO)_{12}$ has been shown[1] to give two types of trinuclear cluster compounds of stoicheiometry $PtFe_2(CO)_8L_2$ (I) and $PtFe_2(CO)_9L$.(II).(II) (L = Ph_3P) has been obtained independently and the i.r. spectrum (cyclohexane solution) confirms the presence of only terminal carbonyl groups.

The molecular structure, shown in the Figure, has been defined by an X-ray analysis of the monoclinic crystals [a = 11·88, b = 14·13, c = 17·47 Å, β = 106·92°; space group $P2_1/c$; 1654 reflexions with $F^2_{\text{obs}}/\sigma(F^2_{\text{obs}}) \geqslant 3{\cdot}0$ (Mo-K_α); R = 0·077; e.s.d.'s average 0·003 Å (Pt–Fe), 0·005 Å (Fe–Fe), and 0·01 Å (Pt–P and Pt–C)]. The absence of bridging carbonyl groups is confirmed and the analysis shows also that the co-ordination around the platinum is quite accurately planar (r.m.s. Δ from mean plane = 0·009 Å); the two independent Pt–Fe bond lengths are significantly different, reflecting the high *trans*-influence[2] of the PPh_3 group relative to that of a carbonyl ligand.

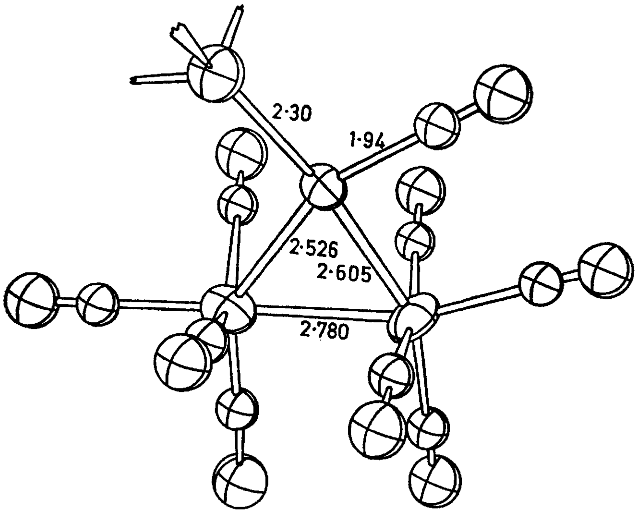

FIGURE. *Stereochemistry of* $Ph_3P(CO)PtFe_2(CO)_8$. *The bond angles around the platinum are* 98·4° (P–Pt–C), 104·5° (P–Pt–Fe), 91·7° (C–Pt–Fe), *and* 65·6° (Fe–Pt–Fe).

The stereochemistry of the cluster suggests that a simple description of the bonding would be a complex of $[Ph_3P(CO)Pt]^{2+}$ with two $[Fe(CO)_4]^-$ moieties. Such a view is also helpful in relating this cluster to similar species such as $RuFe_2(CO)_{12}$,[3] $OsFe_2(CO)_{12}$,[4] $[MnFe_2(CO)_{12}]^-$,[5,6] $[TcFe_2(CO)_{12}]^-$,[6] and $[ReFe_2(CO)_{12}]^-$,[7] which, from the i.r. data, are identical in possessing bridging carbonyl groups and whose structures can be formally derived from that of $Fe_3(CO)_{12}$ by replacing the non-bridged iron atom with the heterometal.[8] All contain, in a formal sense, zerovalent iron as in $Fe_2(CO)_9$.[9] But whereas the nonacarbonyl has three bridging carbonyl groups, $[Fe_2(CO)_8]^{2-}$ has exclusively terminal carbonyl ligands.[10] The broad rationalisation of these results lies in the electroneutrality principle and the greater π-acidity of a terminal carbonyl group compared with its bridging counterpart. In general terms, it is to be expected that the $PtPPh_3(CO)$ fragment is less electronegative than an $Fe(CO)_4$ group and our structural results carry this implication. Other 'mixed' carbonyl clusters containing PtL_2 substituents may have structures which are not predictable so readily by a consideration of the stereochemistry of related systems and this is in keeping with the earlier synthetic and spectroscopic studies.[1]

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[1] M. I. Bruce, G. Shaw, and F. G. A. Stone, *Chem. Comm.*, 1971, 1288.

[2] R. Mason and A. D. C. Towl, *J. Chem. Soc.* (*A*), 1970, 1601.

[3] D. B. Yawney and F. G. A. Stone, *Chem. Comm.*, 1968, 619; *J. Chem. Soc.* (*A*), 1969, 502; J. Knight and M. J. Mays, *Chem. and Ind.*, 1968, 1159.

[4] J. R. Moss and W. A. G. Graham, *J. Organometallic Chem.*, 1970, **23**, C 23.

[5] U. Anders and W. A. G. Graham, *Chem. Comm.*, 1966, 29.

[6] M. W. Lindauer, G. O. Evans, and R. K. Sheline, *Inorg. Chem.*, 1968, **7**, 1249.

[7] G. O. Evans, J. P. Hargaden, and R. K. Sheline, *Chem. Comm.*, 1967, 186.

[8] J. Knight and M. J. Mays, *Chem. Comm.*, 1970, 1006.

[9] H. M. Powell and R. V. G. Ewers, *J. Chem. Soc.*, 1939, 286.

[10] K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc.* (*A*), 1969, 2339.